DPB hydrogen getters on Pd (110) - its action and the effect of impurities

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Abstract

Density Functional Theory (DFT) is used to investigate the action of hydrogen getter 1,4-diphenyl-butadiyne, or DPB, on Pd (110) surface. We study reaction pathways and energetics of several relevant processes, including H_2 adsorption, dissociation and migration on the metal surface, getter-metal interaction, and the energetics of H uptake by the getter. We also explore the effect of impurities like CO and CO_2 on the action of the getter. Activation barriers for certain reactions are computed to shed light on the feasibility of such processes at room temperature.

Introduction

Hydrogen getters are designed to scavenge and store hydrogen in a variety of environments [1, 2]. They are becoming increasingly useful in preventing explosive situations due to hydrogen build up in sealed items such as electronics, heat-exchange equipment, vacuum maintenance, battery-operated devices and so on. Two of the most successful getters so far have been 1,4-bis (phenylethynyl) benzene (DEB) [1, 2] and 1,4-diphenyl-butadiyne (DPB). Both are dialkyne, i.e., each molecule contains two triple bonds (see Fig. 1(a) for DPB), and therefore can uptake four molecules of H_2. Typically these are used in the form of microcrystalline pellets mixed with metallic catalysts like Pd. Previous experiments with DEB indicated that its getting action is unaffected by toluene, hexane, acetone and methanol. However, impurities like CO and a few chlorinated compounds (like carbon tetrachloride, tricholoroethylene, tricholoroethane, choloroform, and methylene chloride) did appear to inhibit or reduce the hydrogen uptake capability [2]. A better understanding of the action of impurities is clearly necessary in order to prevent the loss of getter effectiveness.

While DFT calculations of molecular adsorption on crystal surfaces have now become standard, to our knowledge not much work exists on the action of DEB or DPB getters. This paper discusses our initial calculations with the DPB getters. More specifically we look into H_2 adsorption, dissociation and migration on the metal surface, getter-metal interaction, and the energetics of H uptake by the getter from the metal, as well as the effect of impurities like CO and CO_2 on the action of the getter.

DFT Methodology

For most of our calculations we used the DFT code DMol^3 from Accelrys [3, 4], which employs localized basis sets defined on a numerical grid, and can be used both with molecules and with

periodic supercells, the latter being necessary in this project for representing periodic metal surfaces. Within DMol^3 the electronic wave functions were expanded in a double-numeric polarized (DNP) basis set truncated at a real-space cutoff of 4.0 Å and represented on a "medium" numerical grid. A nonlocal DFT Hamiltonian was used with gradient-corrected exchange-correlation functional due to Perdew, Burke, and Ernzerhof (PBE) [5]. For calculations employing periodic supercells accurate Brillouin zone sampling was ensured by summing over a finite set of K-points chosen according to the Monkhorst-Pack scheme [6] with a grid spacing of 0.05 Å^{-1}. For certain reactions, accurate transition state barriers were obtained by a generalized synchronous transit method recently extended to periodic supercells [7]. For independent verification of some of the binding energy results, we also used the plane-wave code VASP [8] with the PBE functional and "medium" settings.

Molecular models

Fig. 1(a) displays the atomic model of the DPB getter molecule. It consists of two acetylene molecules connected by a single bond and terminated at each end by a phenyl ring. As mentioned earlier, these molecules are usually in the form of powdered crystalline pellets and mixed with metal catalysts like Pd. The H-getting action could happen either by direct dissociation of H_2 on the getter pellet or initial dissociation and chemisorption of H_2 on the Pd surface, followed by the uptake of H by the getter molecules adjacent to the metal surface. In this study we confine ourselves to the second mechanism, which strongly brings out the catalytic action of the Pd surface. For simplicity, we model individual DPB molecules rather than crystallites. Also for concreteness we perform all our calculations on the (110) surface of Pd. The Pd (110) surface was cleaved from the experimental fcc crystal structure of lattice constant 3.89 Å, and was modeled with three atomic layers with the bottom two layers constrained at the bulk position in order to mimic the presence of a larger number of layers in real metal particles. For all simulations of gas adsorption and dissociation on Pd surface a 2x3 extended surface with dimensions of 7.78 Å x 8.25 Å in the surface plane was employed, with a vacuum of 20 Å normal to the plane in order to minimize interaction from translationally periodic images. Computing the binding geometry and energy of the DPB molecule on the metal surface, however, necessitated a more extended 5x4 surface with supercell dimensions of 19.45 Å x 11.00 Å in the surface plane. For investigating binding energies to the getter in gas phase we employed DMol^3 without periodic boundary conditions.
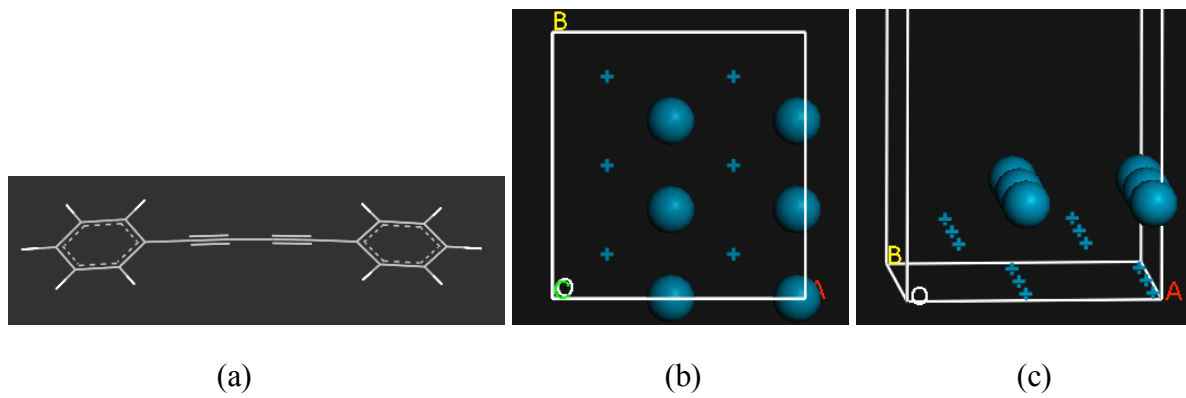

| (a) | (b) | (c) |

Figure 1. (a) Molecular structure of a DPB getter; (b) & (c) Pd (110) 2x3 surface shown in top and side views respectively. The top layer Pd atoms are shown in ball representation for clarity. This layer is allowed to relax in our simulations while the two subsurface layers (atoms shown in cross) are constrained. For simulations of DPB binding a 5x4 Pd (110) surface is used (not shown).

Results

Table 1 lists the computed binding energies of various molecules on the Pd (110) surface, while Table 2 displays the reaction heats (at T = 0) for some of the relevant processes. The main results are summarized below.

Table 1: Binding energy of various species on Pd (110) surface. Computed energy barriers for H_2 dissociation and surface diffusion of H radicals are also indicated.

System	$E_{binding}$ to Pd (110) (kcal/mol)
H_2 (physisorbed)	9.4
H_2 (dissociated)*	16.5
DPB (getter molecule)**	66.0
Benzene	36.5
CO	44.7
COH (alcohol)	19.5
CO_2	4.4

* $\Delta E_{dissociation}^{barrier} \sim 6.4$ kcal/mol, $\Delta E_{diffusion}^{barrier} \sim 6.5$ kcal/mol

**Calculation performed on a (4x5) extended surface

1. Pd (110) surface consists of rows of atoms (along the OB direction in Figs. 1(b) and (c)) with an interatomic separation of 2.75 Å along the rows. The inter-row separation is 3.89 Å. Most energetically stable adsorbate structures occur on the top of a Pd atom or symmetrically above two successive Pd atoms along these rows. In the rest of this paper, these adsorbate configurations are referred to *top-atom* and *mid-row* respectively. For almost all adsorbate structures we find only a small relaxation of the top Pd layer from its unrelaxed as-cleaved geometry.

2. A H_2 molecule physisorbs in the top-atom configuration and has substantial binding ~ 9.4 kcal/mol. It is energetically favorable (by 7.1 kcal/mol) for the H-H bond to break and for the H_2 molecule to dissociate into two H radicals, each bonding in successive mid-row sites along the same row. The dissociation process has a small barrier, 6.4 kcal/mol, which could be easily overcome at room temperature. Each H radical can diffuse easily along the rows, with a

migration barrier of only 6.5 kcal/mol. Migration should also be possible perpendicular to the Pd-rows, likely involving the second-layer subsurface atoms.

3. Most of the binding of the getter molecule to the Pd surface arises out of the strong binding of the end phenyl groups to the metal surface. H_2 uptake happens in the unsaturated bonds of acetylene in the middle. A H_2 molecule gains $43.1 - 16.5 = 26.6$ kcal/mol by moving from the metal surface into an unsaturated bond in the middle of the getter (see Tables 1 and 2), explaining the H_2 scavenging action by the getter.

4. Instead of attacking an unsaturated bond (see point 3 above) a H_2 molecule (or 2 H radicals from the Pd surface) could bind across the phenyl-acetylene bond of the getter, with the latter dissociating into a benzene and a 1-phenyl-butadiyne fragment. Even though this process involves the cleaving of a C-C bond, it is actually an exothermic process in the gas phase (see Table 2).

5. CO binds very strongly to the metal surface in the mid-row configuration, with the C bonding directly to neighboring Pd atoms along a row and the O sticking out normal to the Pd surface as in a carbonyl group [9, 10]. This CO group reacts weakly with freely migrating H radicals on the metal surface. For instance, it does not form a stable aldehyde, and formation of an alcohol is a highly endotermic process (see Table 2). The net binding of a CO group and a H radical in successive mid-row positions along the same row is approximately equal to the sum of binding energies of the individual adsorbates in the absence of the other, which further points to weak interaction between the CO and H.

6. It is difficult to imagine the strongly bound CO leaving the metal surface and chemically attach to the getter. However, it is possible for the O to form a bridge between an unsaturated C of the getter and the original C it was double-bonded to. Such a process would potentially reduce the efficiency of the getter in uptaking H. Further simulations are necessary to investigate the energetic feasibility of this process.

7. Finally, CO_2 interacts weakly with the Pd surface. However, once adsorbed, a CO_2 can interact strongly with a H radical on the metal surface resulting in CO and OH groups bonded to the surface. Such a process is energetically favorable by 25.3 kcal/mol. The OH group can interact with a second H radical and release a water molecule to the atmosphere with a further energy gain of 13.3 kcal/mol.

Table 2: Computed heats of reaction (at T = 0) for relevant processes. Species on metal surface are explicitly indicated. Negative (positive) $\Delta E_{reaction}$ indicates exothermic (endothermic) process.

Reaction	$\Delta E_{reaction}$ (kcal/mol)
H_2 insertion into a DPB (acetylene $\rightarrow$ ethylene)	- 43.1
H_2 (gas) + DPB $\rightarrow$ benzene + 1-phenyl-butadiyne	- 2.5
Pd_CO + Pd_H $\rightarrow$ Pd_COH (alcohol)	+ 33.4

$Pd\_CO_2 + Pd\_H \rightarrow Pd\_CO + Pd\_OH$	- 25.3
$Pd\_OH + Pd\_H \rightarrow Pd + H_2O$ (gas)	- 13.3

Summary and future work

Using the (110) surface of Pd as a concrete model of catalytic metal surface, we investigated the hydrogen scavenging action of DPB getter molecules, and how it could be possibly affected by the presence of poisoning agents like CO and CO_2. The calculations reveal that H_2 should easily dissociate on the Pd surface and the resulting H radicals should diffuse freely. The hydrogen radicals have a strong propensity to saturate the unsaturated bonds in the middle of the getter, explaining the H scavenging action of the getter. Interestingly, it is also energetically feasible for hydrogen to cleave the phenyl-acetylene C-C linkage, and the resulting benzene could be released to the surrounding medium at elevated temperatures. CO adsorbs strongly on the metal surface as well, but interacts weakly with H_2 or the freely diffusing H radicals. However, the adsorbed CO could potentially reduce the effectiveness of the getter in several ways, like: (i) blocking possible binding sites of the getter on the metal surface; and (ii) directly forming a O-bridge with an unsaturated C-atom of the getter. CO_2 binds weakly to the Pd surface, but can potentially lead to the release of H atoms to the surrounding environment in the form water molecules. Further work is necessary to investigate the feasibility of O-bridge formation between the getter and the metal-bound C-atom. Also, other surfaces of Pd (e.g., (111) and (100)) as well as small Pd clusters could present additional bonding situations not present on the (110) surface, and require further thought and simulations.

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